REMARKS

Election/Restriction

Claims 55-57 and 59-132 were present in the examined Application. In the Official Action, the Examiner acknowledged Applicants' election of claim species. By this Reply, Applicants have canceled each of the claims to the non-elected species. Claims 55-57, 59-65, 67-79, 82, 84, 86-92, 97-103, 106, 108, 110-116, and 121-128 are readable on the elected species and remain pending in the Application. Claims 66, 80-81, 83, 85, 93-96, 104-105, 107, 109, 117-120, and 129-132 have been canceled.

Defective Oath or Declaration/Application Data Sheet

The Examiner has indicated the Oath or Declaration is defective for lack of inventor mailing addresses. The Applicants submit herewith an Application Data Sheet containing updated bibliographic data related to the present Application. Applicants request the bibliographic data of the originally filed Oath and Declaration be supplemented with the information provided by the Application Data Sheet. This includes the inventor mailing addresses.

Information Disclosure Statement

Applicants submit herewith a complete copy of the reference, "Catalyst Handbook" 2nd ed., Sections 4.4.1 to 4.11.9 as listed in the information disclosure statement filed on September 10, 2001. Applicants request the reference be considered as to its merits because it was properly cited in the

information disclosure statement before a first Office Action on the merits of the application and only

a portion of the reference was inadvertently left out of the submitted copy.

Specification

The Examiner has objected to the length and content of the Abstract of the disclosure. In this

Reply, Applicants have submitted a replacement Abstract of the disclosure. Applicants submit the

replacement Abstract is in a condition for allowance and request withdrawal of this rejection.

The Examiner has noted three informalities within the Specification. The Specification has

been amended to correct each of these informalities. These amendments are present in the paragraphs

starting at Page 13, Line 9; Page 14, Line 20; and Page 19, Line 13. Applicants submit the

Specification is now in a condition for allowance and request withdrawal of these rejections.

Drawings

In the Drawings, the Examiner has objected to Figs. 2, 5, and 6. Applicants submit herewith

replacement Figs. 2, 5, and 6. In addition, some of the objections to these Figs. are a result of

problems with the Specification, and therefore, portions of the Specification have been amended as

well.

In Fig. 2, the Examiner stated that "P1" does not indicate a reactant flowpath, but rather

indicates the reactor zone, which is also labeled as reactor zone "18." To correct this problem,

Applicants have amended Fig. 2 by clearly indicating "P1" refers to the reactant flowpath as indicated

by the arrows radiating outward from reactor zone 18.

In Fig. 5, the Examiner stated that "P3" does not indicate a reactant flowpath, but rather indicates the same element as indicated by reference numeral 90. To correct this problem, Applicants have amended Fig. 5 by clearly indicating "P3" refers to the reactant flowpath as indicated by the arrows radiating outward from reactor zone 90.

Also with respect to Fig. 5, the Examiner stated that reference numerals 81 and 83 are not present. Applicants believe confusion over the absence of these reference numerals was caused by use of the shorthand "80-84" in the Specification. Applicants have amended the Specification at the paragraph beginning at Page 17, Line 18 by changing "80-84" to "80, 82, and 84."

In Fig. 6, the Examiner stated that "P4" and "116" have been used to designate the same reactant flowpath. To correct this problem, Applicants have deleted reference numeral 116 from Fig. 6. In addition, the Specification has been amended to remove reference numeral 116 from the paragraphs beginning at Page 18, Line 3 and at Page 18, Line 26. Reference numeral 116 is no longer present in the Figs. or Specification.

Also with respect to Fig. 6, the Examiner stated that reference numerals 101, 103, 105, 107, and 109 are not present. Applicants submit confusion over the absence of these reference numerals was caused by use of the shorthand "100-110" in the Specification. Applicants have amended the Specification at the paragraph beginning at Page 18, Line 3 by changing "100-110" to "100, 102, 104, 106, 108, and 110." Applicants submit each of the Figs. is now in a condition for allowance and request notice of the same.

Claim Objections

Claims 55-57, 59-62, 64-67, 69-74, 76-77, 79, 82-84, 86-92, 97-103, 106, 108, 110, 112-116, 121, 123 and 125-128 stand objected to because of informalities. By this Reply, Applicants have canceled claim 66, and amended the remainder of the objected to claims in the manner suggested by the Examiner. Each of these amendments is intended to clarify the claim language rather than to further limit the claims. Applicants submit each of the amended claims is now in a condition for allowance.

Rejections Under 35 USC § 112

Claims 66 and 126 have been rejected as being indefinite for failing to particularly point out and distinctly claim the subject matter which Applicants regards as the invention.

Applicants have canceled claim 66, obviating this rejection.

Applicants have amended claim 126. Amended claim 126 depends from claim 123, and now includes antecedent basis for each of the claim elements. Applicants submit claim 126 is now in a condition for allowance.

Double Patenting Rejections

Claims 55-57, 59-79, 82, 84, 86-92, 97-103, 106, 108, 110-116, and 121-128 have been rejected under the judicially created doctrine of obviousness-type double patenting over claims 1-55 of U.S. Patent No. 6,245,303. Applicants submit that the pending claims are patentably distinct from the claims of the cited patent. In the interest of moving this Application forward, however,
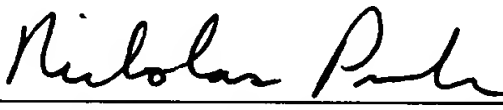
Applicants submit herewith a terminal disclaimer and the required statutory fee of $110 pursuant to

37 C.F.R. § 1.20(d). Applicants submit that this terminal disclaimer addresses the Examiner's double-

patenting rejections, and request the withdrawal of this rejection and the allowance of claims 55-57,

59-65, 67-79, 82, 84, 86-92, 97-103, 106, 108, 110-116, and 121-128. Claim 66 has been canceled.

CONCLUSION

In view of these amendments and remarks, Applicants respectfully submit that the Specification, Figs., and each of the pending claims are in a condition for allowance. Applicants respectfully request that the Examiner withdraw the rejections to each of the pending claims. In the event that any matter in the present application could be addressed by Examiner's Amendment, the Examiner is urged to contact the undersigned attorney.
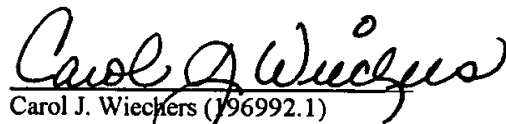
Respectfully submitted,

Date: March 23, 2004

By: _Nicholas Pruhs_

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Date of Deposit: March 24, 2004
I hereby certify that this paper or fee is being deposited with the United States Postal Service under 37 C.F.R. § 1.8 on the date indicated above and is addressed to: Mail Stop FEE AMENDMENT, Commissioner for Patents, PO Box 1450, Alexandria, VA 22313-1450.

Carol J. Wieckers (196992.1)

CATALYST HANDBOOK

SECOND EDITION

Edited by

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Catalytic Systems Division
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P.J.H. Carnell

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Steam Reforming

D.E. Ridler, M.V. Twigg

4. Dust Exposure

Short-term exposure to the metals and metal oxides used in catalysts may give rise to irritation of the skin, eyes and respiratory system. Over exposure can give rise to more serious effects. Product safety data sheets should be consulted for information. Catalysts should be handled as far as possible in well-ventilated areas and in a way which avoids the excessive formation of dust. Operatives who handle catalyst must wear suitable protective body clothing, gloves and goggles. Inhalation of dust should be avoided, and the appropriate occupational exposure limits should be strictly observed. If these limits are likely to be exceeded then respiratory protection should be used. Everyone involved in the handling operation should clean up afterwards and, in particular, must wash before eating. Clothing should be changed at the end of each shift, and more frequently if contamination is heavy.

5. Ergonomics

Hazards associated with the handling of catalysts are discussed in Section 3.3.

Feedstock Purification

4.1. Introduction

The catalysts used in modern ammonia, methanol and hydrogen plants are extremely active and have high selectivity, but they are also very sensitive to poisons. In order to achieve the long production runs required for the economic production of ammonia, methanol and hydrogen it is therefore important to ensure that all of the process fluids are free from poisons, and careful control is required to purify the process water, the process air and the hydrocarbon feedstock. Because of the large volumes of gas passing over the catalysts, small levels of poisons (often at the limit of detection) can have a cumulative effect and restrict catalyst life. A modern ammonia plant is, however, a sensitive analytical instrument, and careful monitoring of catalyst performance will soon show the presence of poisons. The commonest poisons found in hydrocarbon feedstocks are sulphur, chloride and organometallic compounds.

Sulphur is a particularly severe poison for the steam reforming catalyst, which contains nickel. It is adsorbed on the nickel as a surface sulphide and interferes with the steam reforming reaction. The loss of activity can lead to carbon deposition and subsequent overheating of the reformer tubes, which may result in tube failure. The reaction with sulphur is reversible and the reformer will often recover once the source of sulphur is removed. Most steam reformers are designed to be able to operate with a sulphur level of up to 0.5 ppm in the feed, but in practice even this level will cause some loss in activity, and efficient operation demands a level of less than 0.1 ppm. Most modern desulphurization systems will reduce the sulphur content in the feed to less than 0.02 ppm. The onset of sulphur poisoning can be detected by the appearance of hot patches at the top of the reformer tubes. If these are ignored, then the hot patches extend down the tubes and the level of methane in the process gas leaving the reformer ultimately rises.

Chloride is also a serious poison. The chloride ion has high mobility and can migrate freely through the plant with the process gas stream, causing damage to equipment and the catalysts. Many alloy steels are sensitive to chloride induced stress corrosion, and chloride attack causes many heat exchangers to fail. Chloride accelerates the sintering of the

metal crystallites in the catalyst, and this produces an effect similar to thermal ageing but takes place much more rapidly. Chloride will deactivate reforming catalyst, but it is a more serious poison on the copper based low temperature shift and methanol synthesis catalysts. The generally accepted limit for chloride contamination in the feedstock is less than 5 ppb (1ppb = 1 part in 10^9).

Organometallic compounds are common in crude oil (e.g. vanadium porphyrins), but rarely occur in the hydrocarbon feedstocks used on steam reformers. They cause damage by blinding the hydrodesulphuriz-ation and reforming catalysts and, once deposited, cannot be removed. The generally accepted limit for heavy metals is also less than 5 ppb.

4.2. Feedstocks for Ammonia, Methanol and Hydrogen Production

4.2.1. Natural Gas

A wide range of hydrocarbon feedstocks is used for the production of synthesis gas by steam reforming. The most common feedstock now is natural gas. This occurs widely throughout the world, and is the easiest feedstock to process. Natural gas consists mainly of methane, with small amounts of low molecular weight hydrocarbons, and often nitrogen and carbon dioxide. Many natural gases have a low sulphur content which is usually present as simple compounds such as hydrogen sulphide, carbonyl sulphide or mercaptans. In many countries compounds containing sulphur are added to natural gas as a stenching agent to aid in the detection of leaks (e.g. diethyl sulphide in the U.K. and tetrahydrothiophene in The Netherlands). Typical gas compositions for some major gas fields are given in Table 4.1.

Table 4.1. Typical composition of natural gas found in some major gas fields

Component	North Sea	Groningen	Ekofisk	Indonesia
CH_4/%	93.81	81.25	85.45	84.88
C_2H_6/%	4.52	2.83	8.36	7.54
C_3H_8/%	0.38	0.41	2.85	1.60
C_4H_{10}/%	0.04	0.14	0.86	0.03
C_5H_{12}/%	0.02	0.09	0.22	0.12
N_2/%	0.73	14.23	0.43	1.82
CO_2/%	0.47	0.96	1.83	4.0
Total sulphur (H_2S)/ ppm	5	30	2

4.2.2. Associated Gas, Natural Gas Condensates and LPG

Associated gas (the gas released in oil production) is often used as feedstock for ammonia and hydrogen plants located in oil-rich regions such as the Middle East. This gas is very similar to natural gas in that it contains a high level of methane, but it also tends to contain small but variable quantities of high molecular weight hydrocarbons. These may condense in the gas pipeline and arrive at the plant as "slugs" of liquids. Also, associated gas tends to contain significant quantities of hydrogen sulphide and organic sulphur compounds. These factors make associated gas harder to process than natural gas. The variable gas density also makes flow measurement and control difficult, and the high and variable sulphur content may necessitate the inclusion of a sulphur recovery unit to reduce the sulphur content to a reasonable level before it is delivered to a chemical plant. Typical gas compositions for a plant receiving associated gas are given in Table 4.2.[88] The analyses are after treatment on the gas-sweetening plant but before final desulphurization. The total sulphur in the raw gas varies from 1.0% to 3.0% (v/v).

Table 4.2. Variation in composition of associated gas supplied to an ammonia plant in the Middle East[89]

Component	A	B	C	D
CH_4/%	70.75	75.02	73.5	85.04
C_2H_6/%	15.62	14.31	12.3	12.37
C_3H_8/%	7.87	6.02	4.7	2.32
C_4H_{10}/%	3.31	2.51	3.42	0.27
C_5H_{12}/%	1.27	0.78	1.47	0.01
C_6H_{14}/%	0.49	0.23	0.66	
C_7H_{16}/%	0.22	0.03	0.34	
C_8H_{18}/%	0.17		1.49	
C_9H_{20}/%			1.50	
CO_2/%	0.18	0.03	0.03	0.02

A, B and C = variations in associated gas over a 3-year period.

D = gas composition after the installation of a NGL station to remove the heavier hydrocarbons.

Natural gas condensates and LPG consisting of mixtures of ethane through to butane are often used as feedstocks for ammonia plants. These are obtained from the oil-processing industry and are usually fairly pure, with only small amounts of hydrogen sulphide and carbonyl sulphide. However, they can be contaminated with chloride during shipping and storage.

4.2.3. Naphtha

A wide range of naphthas is used, varying from simple light distillate to heavy naphthas with a final boiling point of up to 220°C and containing up to 20% of aromatics. Naphthas are the most difficult feedstocks to purify because they often contain significant quantities of organic sulphur compounds such as thiophenes and benzothiophenes, which are difficult to break down. Although naphtha is not now widely used on a large scale, it is often used as a standby feed. Care is needed in this case to ensure that the purification catalysts can cope with the change from a simple gas duty to naphtha. Many small hydrogen plants use naphtha as their only feed, and because of their small size they have difficulty in obtaining sufficient heat for the purification stage and may not be able to desulphurize certain naphtha feedstocks fully.

4.2.4. Refinery Off Gases and Electrolytic Hydrogen

The high price of hydrocarbon feedstocks has led many operators to use waste gases from refineries. These are generally rich in hydrogen (60–80%) and have a low sulphur content. However, they may contain hydrogen chloride if the refinery uses certain precious metal-based catalytic reforming processes which require the addition of organic chlorides (typically propylene dichloride) to control catalyst activity. They may also contain significant quantities of unsaturated hydrocarbons which can cause processing problems, particularly if acetylenes are present. In a few cases hydrogen obtained by the electrolysis of brine is used as a feedstock. In addition to the risk of chloride contamination this feed may contain mercury, which is particularly harmful to copper-based catalysts.

4.2.5. Coal Gasification and Coke Oven Gas

Ammonia and methanol are also manufacturerd using coal as a feedstock. This is currently limited to countries such as South Africa, Poland, Zambia, India and Turkey which have access to cheap supplies of coal but lack sufficient natural gas. Coal gasification is likely to become more common in the future as supplies of oil and gas are depleted. The gases produced by coal gasification contain both gaseous and solid impurities, and require complex purification trains. The nature of the gas produced is governed mainly by the gasification temperature and, to a lesser extent, by the type of coal. In general, high-temperature gasifiers break down all of the hydrocarbons present, but also produce hydrogen cyanide and nitrogen oxides from the nitrogen compounds present. Low-temperature gasifiers do not produce appreciable quantities of these compounds, but they do yield a range of hydrocarbons and heterocyclic compounds. Table 4.3 gives the reported gas compositions for the Koppers–Totzek gasifier and the Lurgi gasifier which respectively are examples of high- and low-temperature gasification.[89, 90]

Table 4.3. Composition of synthesis gas produced by the gasification of coal in the Koppers–Totzek and Lurgi gasifiers[89, 90]

Component	Koppers–Totzek	Lurgi
CO/%	58.0	20.0
CO_2/%	12.0	29.0
H_2/%	27.0	39.0
N_2 + A/%	1.5	1.0
CH_4/%	<0.1	10.0
C_nH_m/%	NR	0.6
H_2S/%	0.5	0.4
COS/%	0.04	NR
SO_2/ppm	0.1	NR
HCN/ppm	100	NR
NO_x/ppm	30–70	NR
NH_3/ppm	15	NR
O_2/ppm	100	NR
Ash/mg m^{-3}	0.1	NR

NR = not reported.

Coke oven gas is occasionally used as a feedstock. This has a composition similar to feedstocks derived from low temperature gasifiers, but as coke ovens are operated on a cyclic pattern there can be wide variations in gas composition.

4.2.6. Mixed Feeds

Many ammonia and methanol plants now have to be able to use a mixture of different hydrocarbons as feed and fuel. This is perfectly feasible, provided that the full analyses of the feeds are known and the correct purification stages are installed. The different types of feeds and fuel used on one European 1000 tonnes day^{-1} ammonia plant are given in Table 4.4.[91]

Table 4.4. Hydrocarbons used as feedstocks and fuels for a 1000 tonnes day⁻¹ ammonia plant

Feedstock	Fuel
Natural gas	Refinery off-gas
LPG consisting of a 50 : 50 mixture of butane and butene	Fuel oil from an ethylene cracker
Synthesis gas from an oil gasifier	Low-sulphur fuel oil
Hydrogen from an ethylene cracker	LPG (as standby)
Refined naphtha (as standby)	Natural gas (as standby)

4.3. Desulphurization

Sulphur is a poison for nickel steam reforming catalysts, but the poisoning is reversible and in practice there is a threshold limit for given conditions, below which the poisoning effect is not apparent. The sensitivity of the catalyst to sulphur poisoning increases as the reforming temperature is lowered and Figure 4.1 shows the minimum level of sulphur required to poison nickel catalyst in typical industrial steam reformers at different temperatures.[92] Time effects are also important. With very low sulphur levels in the feed to the reformer significant loss of activity is only apparent after quite a long period on line.

Many plants have been able to reverse the effect of a few days of mild sulphur poisoning by switching to a sulphur-free feed, or by steaming the catalysts for a few hours. However, if carbon laydown has taken place it can be difficult to remove the carbon completely from all of the tubes in a reformer. Also, sulphur tends to migrate with the process gases and accumulates on the HT shift and LT shift catalysts, where it can reduce activity. It is far better to prevent sulphur from entering the plant by using an efficient desulphurization system than to have shortened catalyst lives.

4.3.1. Processes for Single-stage Sulphur Removal

Sulphur removal from natural gas by absorption at ambient temperature on activated charcoal or with molecular sieves has been widely used in North America. The active charcoal may have its capacity enhanced by impregnation with transition metals such as copper. Frequent regeneration of the absorbent with steam is required, and two or more
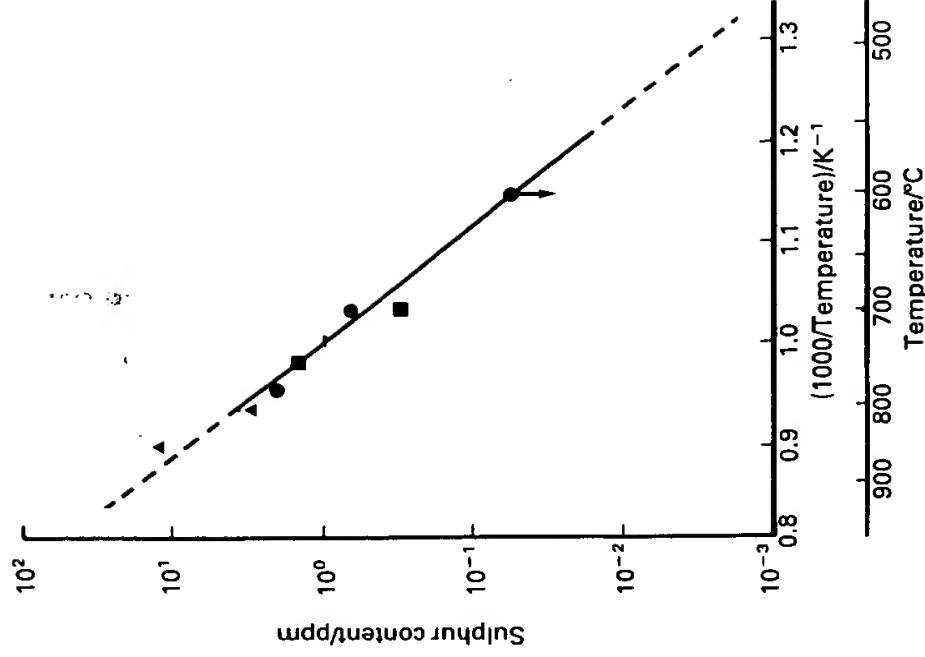
Figure 4.1. The minimum sulphur concentration in process gas to cause practical poisoning of nickel steam reforming catalyst at different temperatures. Hydrocarbon feed: ●, Heptane; ■, naphtha; ▲, methane.

vessels must be available so that one is on-line while the other is being regenerated. The efficiency of these absorbent systems depends both on the type of sulphur compounds and on the amount of high molecular weight hydrocarbons in the natural gas. Low-boiling sulphur compounds such as carbonyl sulphide are not strongly absorbed, and condensable hydrocarbons can rapidly saturate the absorbent. This method of sulphur removal alone has limited application because not all gases can be desulphurized to the level required by a modern high heat flux steam reformer. Also, the regeneration stage requires energy in the form of low-pressure steam, and a malodorous gaseous effluent is produced during regeneration, which can cause environmental problems. If only hydrogen sulphide is present in the natural gas, then it is possible to remove it using zinc oxide. The reaction between hydrogen

sulphide and zinc oxide is covered in detail in Section 4.11 and it is worth noting that this method can effectively remove hydrogen sulphide completely (~0.02 ppm).

4.3.2. Processes for Two-stage Sulphur Removal

Because of the variety of feedstocks in use and the wide range of sulphur compounds encountered, most operators now use a two-stage process for sulphur removal. The first involves reaction with hydrogen to produce hydrogen sulphide and the second is the removal of hydrogen sulphide by reaction with porous zinc oxide. The first stage is carried out using a sulphided cobalt or nickel molybdate catalyst with an excess of hydrogen. If large amounts of hydrogen sulphide are present in the feedstock (either before or after hydrogenolysis), then it may be necessary to remove the bulk of the hydrogen sulphide with a washing stage followed by reaction with zinc oxide. A number of proprietary processes are available. These may also remove carbon dioxide, but they are often not very effective at removing carbonyl sulphide. They involve the use of two packed towers, the first being used for the absorbent medium is an aqueous solution of a weak base such as monoethanolamine (MEA) or diethanolamine (DEA). Regeneration is carried out by heating, usually with a steam-heated reboiler. These processes are simple to operate, and are widely used in the oil processing industry. If large amounts of hydrogen sulphide are liberated in the stripping stage, then it may be necessary to use the Claus process to produce elemental sulphur. This, its simplest form, is shown in equation (1) and the reaction is usually carried out over a promoted alumina catalyst.

$$2H_2S + SO_2 \rightarrow 3S + 2H_2O \qquad (1)$$

The final stage of any modern desulphurization process is a bed (or beds) of granules of high-porosity zinc oxide. Reaction of hydrogen sulphide to give zinc sulphide is favoured under almost all process conditions, and it is possible to reduce the level of hydrogen sulphide in the gas leaving the bed to less than 0.02 ppm. The zinc oxide is of course consumed during the process, and is not regenerable. The bed must be discharged and replaced when it is exhausted, so it may be expensive to use zinc oxide alone to remove high levels of sulphur. The economics vary from plant to plant, but for a typical 1000 tonnes day^{-1} ammonia plant it is not usual to use zinc oxide alone for hydrogen sulphide removal when the feedstock contains sulpur levels above 200 ppm.

4.4. Thermal Dissociation of Sulphur Compounds

Primary and secondary mercaptans decompose at approximately 200–250°C, and tertiary mercaptans decompose at slightly lower temperatures. The products are mainly olefins and hydrogen sulphide, but complex products—including polymers—are also formed. Aromatic thiophenols are generally more stable. Aliphatic disulphides decompose at similar temperatures to mercaptans, giving a mixture of products which usually contain mercaptans and hydrogen sulphide. Aromatic disulphides are more stable and tend to form sulphides and elemental sulphur at approximately 300°C. Cyclic and linear straight-chain sulphides are usually stable up to 400°C, then they decompose to form hydrogen sulphide and olefins. Thiophenes are thermally stable at 470–500°C. Table 4.5 shows the temperatures at which a range of sulphur compounds decompose under the same process conditions. Because of the wide range in thermal stabilities it is quite common for some of the sulphur compounds present in the feedstock to dissociate in the preheater or vaporizer sections of the desulphurization unit before coming into contact with the catalyst. This can lead to carbon and polymer formation on the preheater coils and on the top layer of catalyst. The addition of hydrogen tends to suppress such cracking reactions, and it is always beneficial to add recycle hydrogen before the heating stage.

Table 4.5. Thermal decomposition of selected sulphur compounds

Compound	Temperature at which decomposition commences/°C
$n\text{-}C_4H_9SH$	150
$i\text{-}C_4H_9SH$	225–250
$C_6H_{11}SH$	200
C_6H_5SH	200
$(C_6H_5)_2S$	450
$(C_2H_5)_2S$	400
$C_6H_5SC_6H_{11}$	450
Thiophene	Stable at 500
2,5-Dimethylthiophene	475

4.5. Hydrogenolysis of Sulphur Compounds

The term hydrogenolysis in the present context refers to the addition of hydrogen across a sulphur–carbon bond. The reaction is usually carried out over a nickel or cobalt molybdate catalyst and results in the formation of hydrogen sulphide and a saturated hydrocarbon. Some typical hydrogenolysis reactions for a number of different sulphur compounds are shown in equations (2)-(7). All of these reactions are exothermic but, because of the very low levels of sulphur compounds found in most feedstocks, a temperature rise is seldom observed. Enthalpies of hydrogenation of some typically encountered organic sulphur compounds are given in Table 4.6.
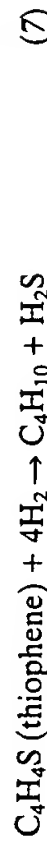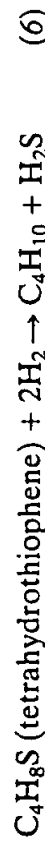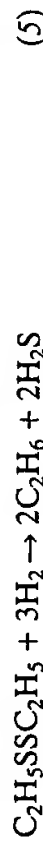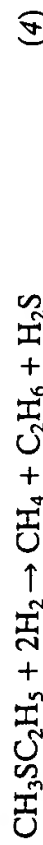
$$C_2H_5SH + H_2 \rightarrow C_2H_6 + H_2S \tag{2}$$

$$C_6H_5SH + H_2 \rightarrow C_6H_6 + H_2S \tag{3}$$

$$CH_3SC_2H_5 + 2H_2 \rightarrow CH_4 + C_2H_6 + H_2S \tag{4}$$

$$C_2H_5SSC_2H_5 + 3H_2 \rightarrow 2C_2H_6 + 2H_2S \tag{5}$$

$$C_4H_8S \text{ (tetrahydrothiophene)} + 2H_2 \rightarrow C_4H_{10} + H_2S \tag{6}$$

$$C_4H_4S \text{ (thiophene)} + 4H_2 \rightarrow C_4H_{10} + H_2S \tag{7}$$
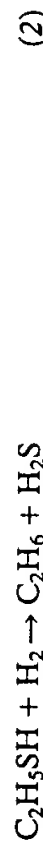
Table 4.6. Heats of hydrogenolysis of some organic sulphur compounds

Reaction	ΔH/ kJ mol^{-1}
$C_2H_5SH + H_2 \rightarrow C_2H_6 + H_2S$	−70.2
$C_2H_5SC_2H_6 + 2H_2 \rightarrow 2C_2H_6 + H_2S$	−117.2
C_4H_8S (tetrahydrothiophene) + 2H$_2$ $\rightarrow n\text{-}C_4H_{10} + H_2S$	−120.2
C_4H_4S (thiophene) + 4H$_2 \rightarrow n\text{-}C_4H_{10} + H_2S$	−280.3

In general, the rate of hydrogenolysis is first-order with respect to the sulphur compound. The order of reaction with respect to the partial pressure of hydrogen lies between zero-order and first-order, depending on the nature of the sulphur compounds present. The equilibrium constants for the hydrogenolysis of organic sulphur compounds are large
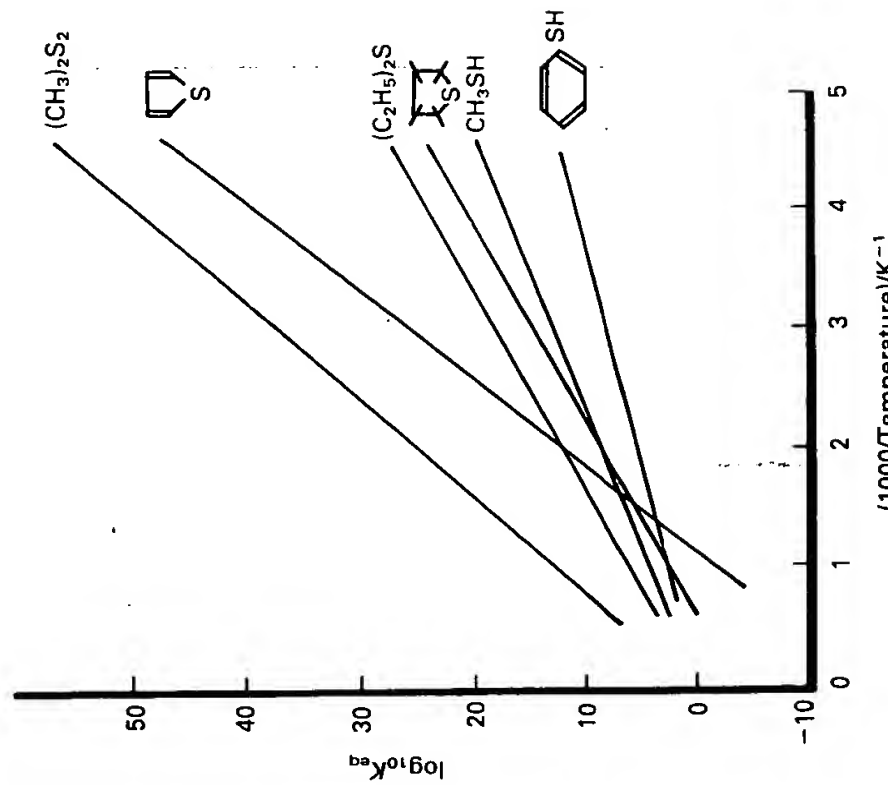
Figure 4.2. The variation of equilibrium constants for the hydrogenolysis of some organic sulphur compounds with temperature.

and positive, even at temperatures as high as 500°C. The rate of hydrogenolysis increases with temperature, and under the usual process conditions between 350°C and 400°C with an excess of hydrogen the hydrogenolysis is normally complete. Figure 4.2 shows the variation of the equilibrium constants for the hydrogenolysis of some sulphur compounds with temperature. There is a marked difference in the rate of hydrogenolysis of thiophene and other commonly found sulphur compounds. This is illustrated in Figure 4.3, which shows the ease of hydrogenolysis of a number of sulphur compounds using a heptane feed at atmospheric pressure and 370°C and 250°C.

Rate constants for hydrogenolysis of a particular sulphur compound are dependent on the types of hydrocarbon present. Diffusion of sulphur compounds is easier through low molecular weight hydrocarbons than through those of high molecular weight, and the rate of hydrogenolysis is therefore faster the lower the molecular weight of

4.6. Carbonyl Sulphide

Carbonyl sulphide (COS) is usually present in natural gas which contains carbon dioxide and hydrogen sulphide. Carbonyl sulphide has a low boiling point (−50°C) and is therefore not easy to remove with fixed-bed absorbents such as active charcoal or molecular sieves, and it can be a source of sulphur poisoning. Carbonyl sulphide is thermally stable and it may not be fully hydrogenolysed over cobalt molybdate catalyst. This is because of what may be called the "reverse water-gas shift" reaction which is catalysed by cobalt molybdate catalysts, and so limits the extent of conversion. Carbonyl sulphide leaving the cobalt molybdate catalyst will react with zinc oxide, but the rate of reaction is slow and the absorption profile shallow, so a conventional desulphurization system will not fully remove carbonyl sulphide.[93] However, it has been shown that carbonyl sulphide is rapidly hydrolysed by steam to carbon dioxide and hydrogen sulphide as in equation (8), and the level of carbonyl sulphide leaving the cobalt molybdate catalyst can be controlled by steam addition. The steam requirement can be calculated from equation (9) using the data in Table 4.7. The hydrolysis reaction is fast over cobalt molybdate catalyst, and plants with high levels of carbonyl sulphide in the feed gas can use steam hydrolysis with confidence.

$$COS + H_2O \rightleftharpoons CO_2 + H_2S \tag{8}$$

$$K = \frac{P_{H_2S}\, P_{CO_2}}{P_{COS}\, P_{H_2O}} \tag{9}$$

Table 4.7. Equilibrium constants for the hydrolysis of carbonyl sulphide

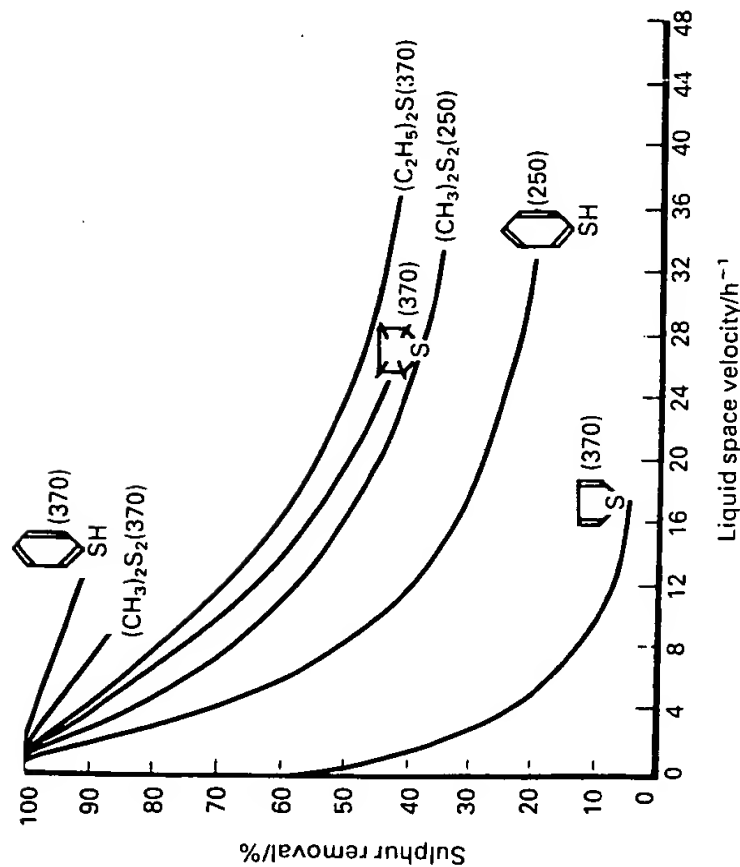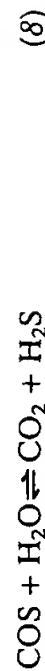| Temperature/°C	K_p
25	7.2×10^5
125	2.23×10^4
225	2.86×10^3
325	719
425	268

Figure 4.3. The desulphurization of heptane using a cobalt molybdate catalyst (atmospheric pressure at 250°C and 370°C, hydrogen/heptane ratio 1 : 4).

the hydrocarbon. Also, hydrocarbons are absorbed on the cobalt molybdate catalyst, and those with high molecular weight are more firmly held, so inhibiting the hydrogenolysis reaction. Olefins are hydrogenated exothermically over cobalt molybdate catalyst, but if insufficient hydrogen is present for complete hydrogenation it is possible for hydrogen sulphide produced at the top of the bed to add across the double bond to form an organic sulphur compound. Nowadays, because naphtha is rarely used as a feed, complex sulphur compounds seldom have to be treated in the desulphurization unit. With process conditions largely set by the zinc oxide bed and the primary reformer catalyst, it is rare to encounter any problems with the hydrogenolysis stage of the desulphurization process. In practice, if unreacted sulphur compounds are reported in the gas leaving the hydrodesulphurizer the two most common explanations are analytical error or mechanical damage to the catalyst bed which had given rise to channelling, so allowing some process gas to by-pass the catalyst in the reactor.

4.7. Cobalt Molybdate Catalysts

Cobalt molybdate is the most widely used catalyst for the hydrogenolysis of sulphur compounds. It has been the subject of much research work over recent years, but since its discovery many years ago its composition has changed little. The main development has been the change from "premixed" to impregnated catalysts. Modern cobalt molybdate catalysts use a special alumina support which is characterized by a highly porous structure. The internal surface area is typically between 200 m^2 g^{-1} and 400 m^2 g^{-1}. The alumina support is impregnated first with a molybdenum compound and then with a cobalt compound and then processed to give a mixture of complex oxides. The total amount of molybdenum and cobalt present varies according to the formulation, but the amount of molybdenum oxide (MoO$_3$) is usually three to four times the amount of cobalt oxide (CoO). In the oxide form the catalyst consists of a "thin layer" of MoO$_3$ bonded to the alumina support, with cobalt held in the upper lattice planes. There is speculation about the active phase or phases. The fresh catalyst has been shown to contain Al$_2$O$_3$, CoAl$_2$O$_4$, CoO, MoO$_3$, CoMoO$_4$ and a complex cobalt molybdenum oxide. The relative proportions of these compounds depends on the nature of the support and the firing temperature used during manufacture. The higher the firing temperature, the greater the content of CoAl$_2$O$_4$. The composition of a typical commercially available cobalt molybdate catalyst (ICI Catalyst 41-6) is given in Table 4.8.

Table 4.8. Composition and properties of a typical cobalt molybdate catalyst (ICI Catalyst 41-6)

CoO	4.0%
MoO$_3$	12.0%
SiO$_2$	1.0%
Al$_2$O$_3$	Balance
Bulk density	0.6 kg l^{-1}
Surface area	220 m^2 g^{-1}
Pore volume	0.6 ml g^{-1}

Cobalt molybdate catalysts have low activity in the oxide form, and to obtain maximum activity they must be sulphided. The composition of the sulphided form is related to the oxide form, but because the sulphiding is carried out in a reducing atmosphere there is some

reduction in the oxidation state of the molybdenum ions. It is found in practice that between one and two sulphur atoms are taken up by each molybdenum ion, and water is liberated by condensation of neighbouring hydroxyl groups.

Despite many studies there is still no universal agreement on the nature of the active sites in cobalt molybdate catalyst. It is generally agreed that the active sites are those with sulphur vacancies. It seems likely that these sites contain cobalt atoms present in the MoS$_2$-like Co–Mo–S phase. The role of the cobalt ions is not clear, but it is assumed that they promote the activity of the molybdenum sulphide. Work on the reactions taking place on cobalt molybdate catalyst is complicated by the highly mobile nature of part of the sulphur. The degree of sulphiding depends on the partial pressure of hydrogen sulphide in the feed, and it is possible for hydrogen sulphide to be released from the catalyst when changing from a feed with a high sulphur content to one with a low sulphur content. Discharged cobalt molybdate catalysts from ammonia or methanol plants usually contain between 0.5% and 3.0%(w/w) of sulphur. The higher value is only found if the catalyst is being used for desulphurizing a feed with a high sulphur content, e.g. a "dirty" naphtha.

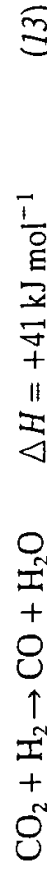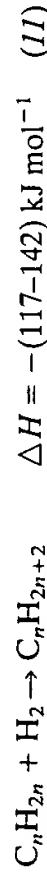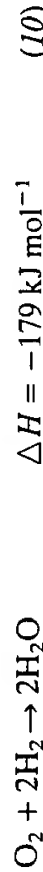### 4.7.1. Presulphiding Cobalt Molybdate Catalyst

If sulphur is not always present in the feedstock it may be necessary to presulphide the catalyst before bringing it into service. This is carried out using an easily decomposed sulphur compound, such as carbon disulphide, dimethylsulphide (DMS), dimethyldisulphide (DMDS) or even hydrogen sulphide. The reaction is carried out using nitrogen, methane or the normal feed as a carrier. For presulphiding it is usual to use about 1% of the sulphur compound and 5%(v/v) of hydrogen. The reaction is exothermic and these conditions will produce a temperature rise of about 10°C. Care must be taken not to exceed bed temperatures of 300°C until sulphiding is complete. This is to avoid the risk of "over-reducing" the oxides in the catalyst. Once formed, metal does not easily sulphide and the catalyst will not then gain full activity. Sulphiding can be carried out during a normal start-up, but is must be remembered that the feed may not have sufficient sulphur to activate the catalyst fully until after many days of operation.

Hydrogenolysis reactions are carried out over cobalt molybdate catalysts at temperatures between 280°C and 400°C. The catalyst is not normally active enough at lower temperatures, and there is the risk of hydrocarbon cracking at higher temperatures. The reaction pressure is normally set by the inlet pressure to the reformer, and most

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hydrodesulphurization reactors in ammonia and methanol plants work in the range 30–50 bar. The space velocity used depends on the feed and the type of sulphur compounds present, but most plants operate with space velocities of less than 3000 h^{-1}. The reaction needs hydrogen, but the level used is normally set by the need to suppress hydrocarbon cracking and by that required for the primary reformer. Most plants using natural gas work with an inlet hydrogen content of 2–5%, while those using naphtha work with ~25%. The larger excess of hydrogen used with naphtha is mainly to suppress cracking reactions.

4.7.2. Other Reactions over Cobalt Molybdate Catalyst

When sulphided, cobalt molybdate catalysts promote most hydrogenation reactions. This means that a number of side reactions can take place over the catalyst, and operators need to consider possible reactions of all of the components in the feedstock. Some of these reactions are shown in equations (10)-(13).

$$O_2 + 2H_2 \rightarrow 2H_2O \qquad \Delta H = -179 \text{ kJ mol}^{-1} \qquad (10)$$

$$C_nH_{2n} + H_2 \rightarrow C_nH_{2n+2} \qquad \Delta H = -(117\text{–}142) \text{ kJ mol}^{-1} \qquad (11)$$

$$CO + 3H_2 \rightarrow CH_4 + H_2O \qquad \Delta H = -219 \text{ kJ mol}^{-1} \qquad (12)$$

$$CO_2 + H_2 \rightarrow CO + H_2O \qquad \Delta H = +41 \text{ kJ mol}^{-1} \qquad (13)$$

With the exception of the reverse water-gas shift reaction (13) all of these reactions are exothermic and can cause a significant rise in temperature across the catalyst bed. A typical natural gas feed containing only 0.8% of unsaturated hydrocarbons would give a temperature rise of 20°C (equation (11)). If the feed contains a high level of unsaturated hydrocarbons it will be necessary to hydrogenate in a separate recycle loop with a heat exchanger to deal with the exotherm. One operator has successfully run a 1000 tonnes day^{-1} ammonia plant using a feed with 40–50% butene in this way.[91] Olefins present another problem, since if they are not fully saturated they can react with hydrogen sulphide to form organic sulphides which will not be retained on the zinc oxide bed. Acetylenes pose a particular problem because they tend to polymerize to form high molecular weight compounds over cobalt molybdate catalyst. These block the catalyst pores and can lead to a rise in the pressure drop across the bed. Low concentrations of acetylene (200 ppm) have been found to cause so much polymer deposition that a bed of cobalt molybdate catalyst had to be changed after only a few months of operation.[88]

Oxygen is not normally encountered in natural gas, but can be present if air is injected to reduce the calorific value of a rich gas. It can cause

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problems with cobalt molybdate catalyst: if insufficient sulphur is present to sulphide the catalyst, sulphur may be converted to sulphur dioxide which is not retained by hot zinc oxide.

4.8. Nickel Molybdate Catalysts

Cobalt molybdate catalysts are the most widely used hydrogenolysis catalysts, but there are certain process conditions under which they cannot be used (in particular, where there are very high levels of hydrogen and carbon oxides). These conditions can be encountered on methanol plants and town-gas plants when process gas is used as a source of hydrogen. It is possible under certain circumstances for cobalt molybdate catalysts to promote the methanation reaction (equation (12)) and, because of the large amount of heat released, there can be a very large rise in temperature. For these duties sulphided nickel molybdate catalyst is recommended, because once sulphided there is a much smaller risk of the methanation reaction taking place. Nickel molybdate catalyst behaves in a similar way to cobalt molybdate catalyst, but it is a slightly more powerful hydrogenation catalyst and can cause more hydrocracking. The composition of a typical commercially available nickel molybdate catalyst (ICI Catalyst 61-1) is given in Table 4.9.

Table 4.9. Composition and properties of a typical nickel molybdate catalyst (ICI Catalyst 61-1)

NiO	3.8%
MoO$_3$	11.8%
SiO$_2$	1.8%
Al$_2$O$_3$	Balance
Bulk density	0.6 kg l^{-1}
Surface area	220 m^2 g^{-1}
Pore volume	0.6 ml g^{-1}

4.9. Physical Form of Cobalt and Nickel Molybdate Catalysts

Catalyst manufacturers have developed a number of different shaped catalysts which increase the geometric surface area of the catalyst, and so increase the reactivity. These are used for hydrotreating in refineries where high activity is required. The increased activity is obtained at the

cost of greater resistance to flow, and hence a higher pressure drop across the bed. Usually in ammonia and methanol plants the hydrodesulphurization reaction is not kinetically limited. Most ammonia and methanol plant operators use catalyst in the form of simple extrudates with a nominal diameter of ~3 mm. In this form the catalyst has high enough activity for the desulphurization needed and in addition the pressure drop is low (usually less than 3 psig). Refinery operators need higher activity and usually use extrudates with a nominal diameter of ~1.5 mm. They may also use multilobe extrudates, or even extrudates with diameters of ~1 mm. Special catalysts may be used for demetallization operation. These are mechanically stronger and have a greater absorption capacity. Because of the variety of shapes available, operators should be careful when replacing the catalyst to use the same form. Change in physical form may increase the catalyst activity, but it may also significantly increase pressure drop across the bed.

4.10. Replacement and Discharging of Cobalt and Nickel Molybdate Catalysts

Both nickel and cobalt molybdate catalysts can give long lives, and rarely have to be changed because of loss of activity. The most usual reason for changing the catalyst is because of an increase in pressure drop resulting from carbon deposition. The carbon is usually formed as a fine dust in the gas preheater section and is carried forward onto the catalyst. Unsaturated hydrocarbons may polymerize on the catalyst to give tarry deposits. The catalyst can still operate with surprisingly high levels of carbon—up to 10% causes little problem and levels up to ~30% have been observed. It is possible to regenerate the catalyst by burning off the carbon with a steam/air mixture, but this is a very exothermic reaction and few plants have the necessary instrumentation to carry out the operation in a sufficiently well controlled manner. It is therefore usually recommended that the top layer of contaminated catalyst be removed and replaced with fresh material.

Used cobalt and nickel molybdate catalysts are potentially pyrophoric in air, and it is advisable to cool them to below 50°C before they are discharged. It is also advisable to use an inert atmosphere for their vacuum discharge. The pyrophoricity is probably due more to the presence of fine carbon dust, residual hydrocarbons and chemisorbed hydrogen than to the cobalt, nickel and molybdenum sulphides, although in some circumstances high area metal sulphides undergo rapid oxidation to the corresponding sulphate.

4.11. Zinc Oxide

4.11.1. Background to Zinc Oxide Absorbents

For many years hydrogen sulphide was removed by absorption in beds of iron oxide. This was loaded in the form of Fe_2O_3, and then converted in the presence of hydrogen at temperatures above 175°C into Fe_3O_4 as in reaction (14). Absorption of hydrogen sulphide was carried out at 350–400°C according to reaction (15).

$$3Fe_2O_3 + H_2 \rightarrow 2Fe_3O_4 + H_2O \qquad (14)$$

$$Fe_3O_4 + H_2 + 3H_2S \rightarrow 3FeS + 4H_2O \qquad (15)$$
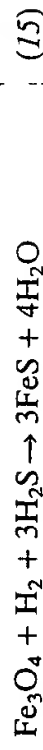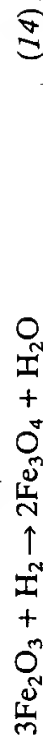
Iron oxide is a low-cost material and has a high absorption capacity, but it is not a suitable absorbent to use for desulphurizing the feed to a steam reformer. This is because at equilibrium the partial pressure of hydrogen sulphide is too high—see Table 4.10. Also, hydrogen sulphide is relatively easily stripped by hydrogen and steam under conditions which may arise during start-up and shutdown of the plant. The final absorption stage in modern synthesis gas plants is carried out using beds of zinc oxide. Zinc oxide reacts almost completely with hydrogen sulphide to form zinc sulphide as shown in equation (16).

$$ZnO + H_2S \rightarrow ZnS + H_2O \qquad (16)$$

4.11.2. Thermodynamics and Reaction Kinetics

The thermodynamic effects of water vapour on the efficiency of iron oxide and zinc oxide for the absorption of hydrogen sulphide are shown in Tables 4.10 and 4.11, and the equilibrium constants for equation (16) over a range of temperatures are given in Table 4.12. The exact values for the equilibrium constants depend on the form of zinc sulphide produced and this is discussed in Appendix 20.

Kinetic studies[95] of the reaction of hydrogen sulphide with powdered zinc oxide have shown that the reaction is first-order with respect to the hydrogen sulphide concentration, with a rate constant given by equation (17).

$$k = 9.46 \times 10^{-2} \exp(-7236/RT) \qquad (17)$$

In the reaction between hydrogen sulphide and zinc oxide the hydrogen sulphide molecules must first diffuse to the surface of the zinc oxide. There H_2S reacts with the zinc oxide to form zinc sulphide, and the

Table 4.10 The effect of water vapour and temperature on the equilibrium H_2S concentration over iron oxide, based on equation (15) for gas containing 20% hydrogen

	Equilibrium H_2S concentration/ppm(v/v)				
H_2O/%	200°C	250°C	300°C	370°C	400°C
3.3	1.85	3.1	5.1	8.9	10.8
1.7	7×10^{-1}	1.35	2.02	3.51	4.23
0.33	0.85×10^{-2}	1.57×10^{-1}	2.02×10^{-1}	4.1×10^{-1}	4.9×10^{-1}
0.17	1.57×10^{-3}	0.62×10^{-1}	0.93×10^{-1}	1.64×10^{-1}	1.96×10^{-1}

Table 4.11 The effect of water vapour and temperature on the equilibrium H_2S concentration over zinc oxide, based on equation (16) for gas containing 20% hydrogen

	Equilibrium H_2S concentration/ppm(v/v)				
H_2O/%	200°C	250°C	300°C	370°C	400°C
3.3	2.6×10^{-4}	1.7×10^{-3}	0.7×10^{-2}	4.2×10^{-2}	6.5×10^{-2}
1.7	1.3×10^{-4}	0.9×10^{-3}	0.3×10^{-2}	2.1×10^{-2}	3.2×10^{-2}
0.33	2.6×10^{-5}	1.7×10^{-4}	0.7×10^{-3}	4.0×10^{-3}	6.5×10^{-3}
0.17	1.3×10^{-5}	0.9×10^{-4}	0.3×10^{-3}	2.0×10^{-3}	3.3×10^{-3}

Table 4.12. Gas phase equilibrium constants for the reaction of zinc oxide with hydrogen sulphide (see also Appendix 20)

Temperature/°C	$K_p = P_{H_2O}/P_{H_2S}$
200	2.081×10^8
260	2.359×10^7
300	7.121×10^6
360	1.569×10^6
400	6.648×10^5
460	2.185×10^5
500	1.145×10^5

water formed must diffuse away. Finally, the sulphide ion must diffuse into the lattice, and oxide ions diffuse to the surface. The conversion of the hexagonal zinc oxide structure into cubic zinc sulphide involves severe structural changes, and the incorporation of the much larger sulphide ion in place of the oxide ion results in a marked loss in porosity. Under normal conditions the equilibrium is strongly in favour of sulphide formation, but the factors discussed above mean that the overall rate of the reaction is controlled by both pore diffusion and

lattice diffusion. As a result of these effects, all of the zinc oxide may not be converted to sulphide in a sensible time.

4.11.3. Formulation of Commercial Zinc Oxide

The factors discussed in the previous section have to be taken into account in the formulation of zinc oxide absorbents. The dependence on lattice diffusion can be reduced by making a highly porous zinc oxide with a large internal surface area. However, such a material would have a low density and little mechanical strength. The low mechanical strength would make handling difficult, and the low density would mean that the theoretical sulphur pick-up on a volume basis would be low. Strength and density can be increased by compaction, but such material would have a low porosity with a low surface area, and the rate of reaction with hydrogen sulphide would be correspondingly low. ICI recognized this problem and does not attempt to make a zinc oxide absorbent using zinc oxide alone. Instead, ICI's zinc oxide absorbent (Catalyst 32-4) consists of zinc oxide with a small amount of cement support. This approach enables a high porosity to be obtained whilst maintaining physical strength, ensuring good utilization of the zinc oxide. A typical composition of ICI Catalyst 32-4 is given in Table 4.13. This material can absorb up to 30%(w/w) of sulphur (measured in discharged catalyst). Zinc oxide is also produced in the form of extrudates. These are more difficult to handle because the extrudates tend to interlock and resist flow during charging. The angle of repose for granular zinc oxide is 32° while that for extrudates is typically 38°. Section 4.11.5 contains a discussion on enhanced low temperature activity zinc oxide.

Table 4.13. Typical analysis and properties of zinc oxide granules (ICI Catalyst 32-4)

ZnO	90.0%
CaO	2.0%
Al_2O_3	Balance
Surface area	25 m² g⁻¹
Bulk density	1.1 kg l⁻¹
Diameter	3.0–5.0 mm

4.11.4. Use of Test Reactors to Assess Zinc Oxide Absorbents

Large beds of zinc oxide are used on the commercial scale in order to ensure long lives, and hence they are not suitable as test reactors. It is, however, possible to study the efficiency of sulphur removal using small

laboratory reactors. The most satisfactory procedure is to use the test reactor to compare different zinc oxides rather than to obtain absolute measurements.

For example in a typical experiment a small laboratory reactor was filled with a mixture of equal volumes of two zinc oxides. An operating temperature of 370°C and a gas pressure of 30 bar were used, so the conditions of the test were similar to those encountered in industrial reactors. Natural gas containing hydrogen and hydrogen sulphide was passed through the reactor until hydrogen sulphide was detected in the exit gas. The mixed bed was then discharged in layers, and the sulphur
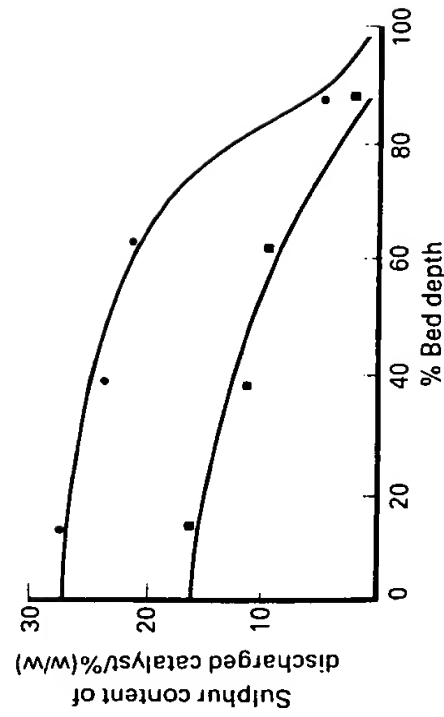
Figure 4.4. Sulphur absorption profiles for ●, ICI Catalyst 32-4 and ■, high-density zinc oxide. Test conditions: temperature, 370°C; pressure, 30 bar; feed, natural gas; space velocity, 400 h^{-1}.

absorption profiles shown in Figure 4.4 were obtained by chemical analysis. The sulphur distribution within individual pellets was determined by different techniques. A small amount of hydrogen sulphide containing the radioactive isotope ^{35}S had been included with the hydrogen sulphide. This allowed the set of autoradiographs shown in Figure 4.5 to be obtained from split pellets of the discharged zinc oxide sampled from different parts of the bed. The material from the inlet is at the top and that from the exit at the bottom. The same split pellets were also examined using an electron microprobe analyser. This gave the photomicrographs shown in Figure 4.6. The electron microprobe is less affected by surface preparation, and gives a more quantitative picture of the absorption pattern across the pellets than is possible with the autoradiographs. The electron microprobe is able to detect sulphur levels greater than ~0.1%(w/w). These two techniques give an interesting indication of the way in which the sulphur is absorbed from the outside of the pellet towards the inner core. They also show that if the zinc oxide is too dense, an impervious layer of zinc sulphide is
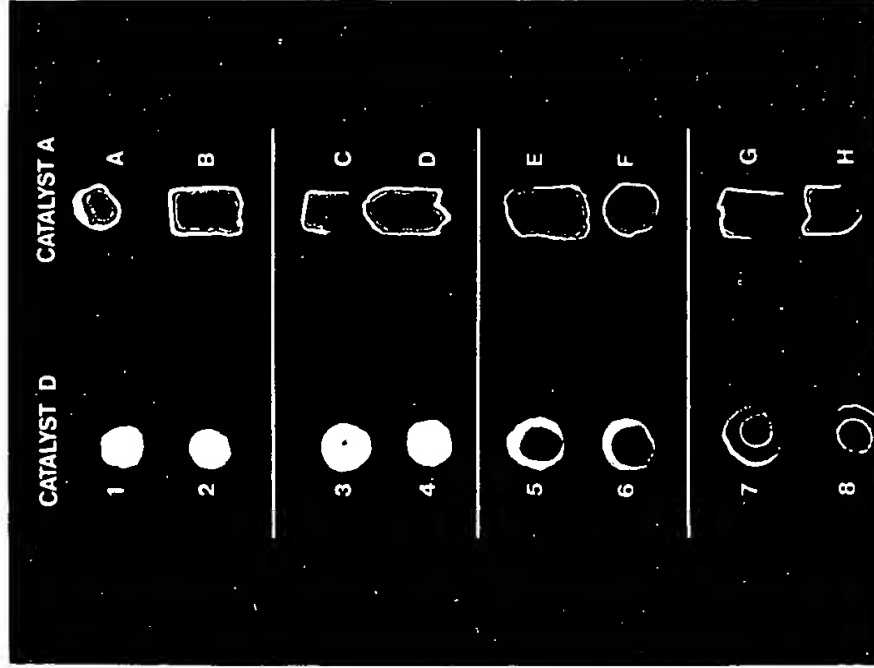
Figure 4.5. Autoradiographs showing the distribution of sulphur within individual pellets of zinc oxide. Pellets 1 and A at bed inlet, 8 and H at bed exit.

formed around the pellets which makes utilization of the inner core difficult.[96,97]

4.11.5. Effect of Temperature, Pressure and Space Velocity on Efficiency of Zinc Oxide Absorbents

The strong dependence on pore and lattice diffusion leads to the performance of zinc oxide being affected by the process conditions. Because of the high activation energy of the lattice diffusion process, the efficiency of absorption falls rapidly as the temperature is reduced. Figure 4.7 shows the average sulphur content of a bed of zinc oxide in a test reactor at the moment of sulphur slip at different temperatures using the same hydrocarbon feed. It can be seen that for efficient utilization the bed needs to be kept above 350°C. Zinc oxide will react with hydrogen sulphide up to 700°C, but at high temperatures zinc metal
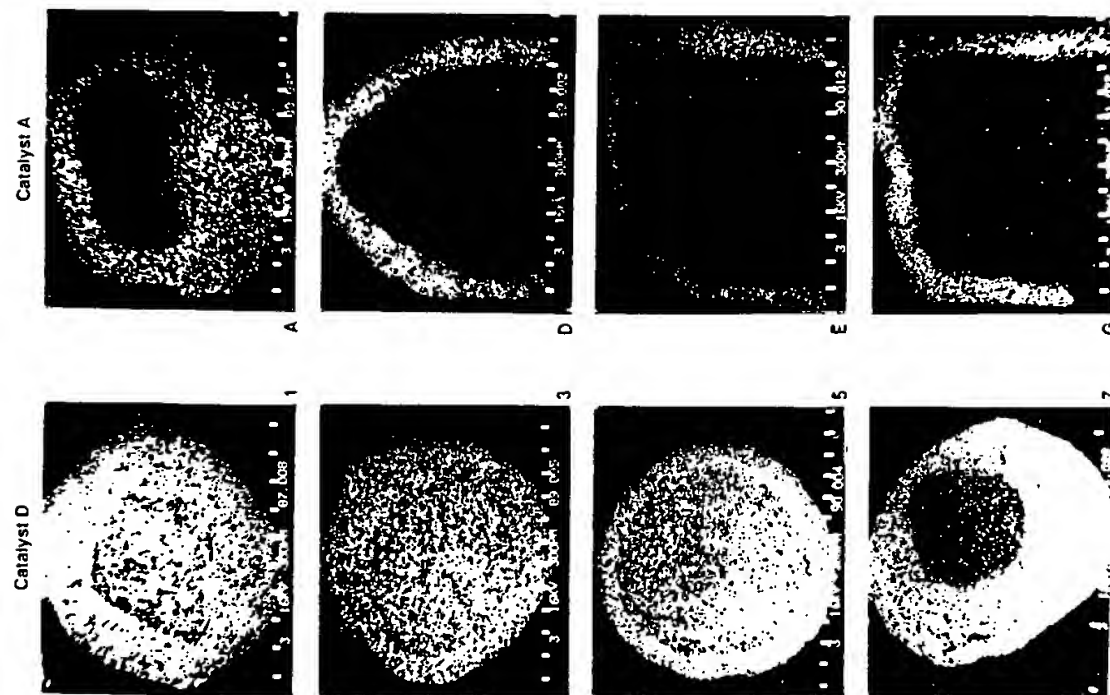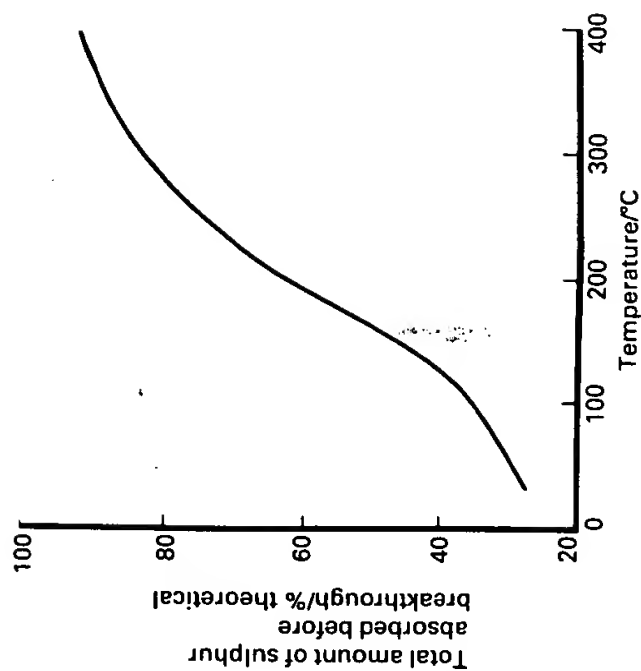
Figure 4.7. The effect of temperature on the absorption of hydrogen sulphide by zinc oxide (ICI Catalyst 32-4). Test conditions: pressure, 30 bar; feed; light hydrocarbon; space velocity, 400 h^{-1}.
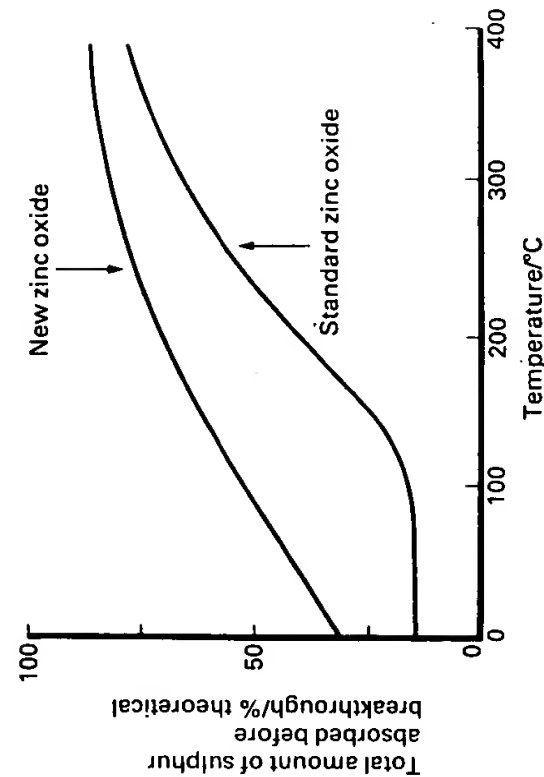

Figure 4.8. A comparison of low-temperature zinc oxide (ICI Catalyst 75-1) with conventional zinc oxide (ICI Catalyst 32-4). Pressure, 1 bar; feed, natural gas; 4% CO_2; 0.2% H_2S.

Figure 4.6. Electron microprobe photographs showing the distribution of sulphur within some of the pellets of zinc oxide in Figure 4.5.

starts to be formed. In spite of the low efficiency of sulphur pick-up at low temperatures, zinc oxide is in use in plants down to ambient temperatures. Attempts have been made to improve the low-temperature performance of zinc oxide, and it has been found that the inclusion of certain metals does result in improved absorption. A recently developed commercial zinc oxide (ICI Catalyst 75-1) which has greatly improved low-temperature activity[98] has been achieved by adjusting both the pore structure and the surface area. The enhanced low-temperature activity compared with normal zinc oxide is shown in Figure 4.8.
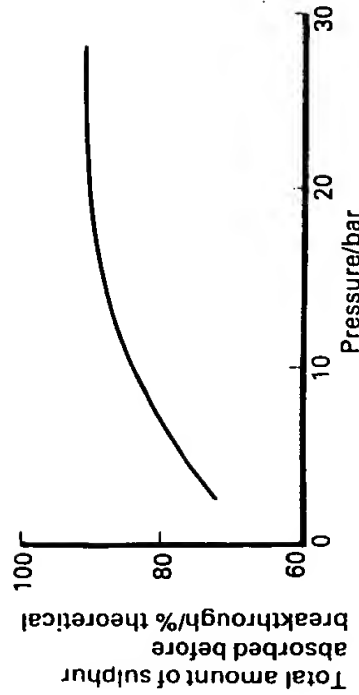
Figure 4.9. The effect of pressure on the absorption of hydrogen sulphide by zinc oxide (ICI Catalyst 32-4). Test conditions: temperature, 370°C; feed, light hydrocarbon; space velocity, 400 h⁻¹.

Pressure has a small effect on the operation of zinc oxide beds. There is a slight reduction in achieved sulphur pick-up below ~10 bar, but from 3 bar to 100 bar performance is unchanged. Figure 4.9 shows the variation in pick-up in the pressure range 1–30 bar using ICI Catalyst 32-4 under typical operating conditions. However, pressure does have an effect if the feedstock contains gases which can condense in the micropores of the zinc oxide. In this case there is then an additional diffusion limitation which slows the reaction of hydrogen sulphide with zinc oxide at the centre of the pellet. Also, at high space velocities (above 4000 h⁻¹) the absorption profile is sharper the greater the pressure. Space velocity influences the degree of absorption because it governs the contact time. Figure 4.10 shows the relationship between space velocity and sulphur absorption capacity using a naphtha feedstock at 20 bar and 370°C. Zinc oxide absorbents were developed to desulphurize the hydrocarbon feedstocks used for steam reformers, and the process conditions on most plants are within the range given in Table 4.14.

Table 4.14. Normal operating conditions for zinc oxide

Temperature	370–400°C
Pressure	20–40 bar
Space velocity	500–1000 h⁻¹
Bed height/diameter ratio	1 : 1

4.11.6. Effect of Gas Composition

The composition of the feedstock also affects the sulphur absorption profile. A very sharp profile is obtained when hydrogen is the process gas. The profile with methane is almost as sharp as with hydrogen, but
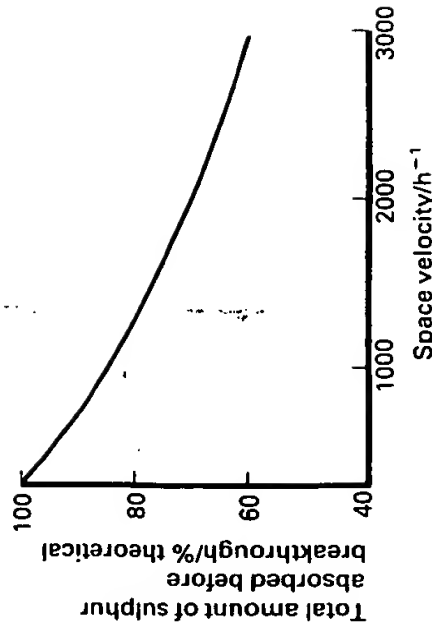

Figure 4.10. The effect of space velocity on the absorption of hydrogen sulphide by zinc oxide (ICI Catalyst 32-4). Temperature, 370°C; pressure, 20 bar; feed, light hydrocarbon; 300 ppm H₂S, 25%(v/v) H₂.

high molecular weight hydrocarbons give a shallower profile. This is because of physical blocking of the capillaries, which causes an additional hindrance to the diffusion process. Carbon dioxide can also interfere with the absorption reaction. Zinc carbonate is stable at temperatures below about 160°C (dependent on the partial pressure of carbon dioxide). Hydrogen sulphide displaces carbon dioxide from zinc carbonate, but at low temperatures these are clearly competing reactions and absorption efficiency may be reduced.

4.11.7. Effect of Reactor Design

The conversion of zinc oxide to zinc sulphide gives an absorption profile which passes down the bed, and a zinc oxide charge is considered to be spent when hydrogen sulphide slip above 0.1 ppm is observed. The shape of the absorption profile is governed by the process conditions and the properties of the zinc oxide, so the efficiency of utilization for any given process conditions and absorbent depends on the height-to-diameter ratio of the zinc oxide bed. Increasing the bed depth does increase the pressure drop, but as the pressure drop is very low for the space velocities normally used, tall thin beds are more practical than is generally realized. Figure 4.11 shows the relationship between pressure drop and height-to-diameter ratio for a 20 m³ charge of ICI Catalyst 32-4 on a typical 1000 tonnes day⁻¹ ammonia plant with natural gas feed. The static crush strength of ICI Catalyst 32-4 has been tested, and there is no evidence of breakdown at pressures equivalent to beds 15 m deep. Beds are already in service with depths up to 10 m, and deeper beds are being considered.

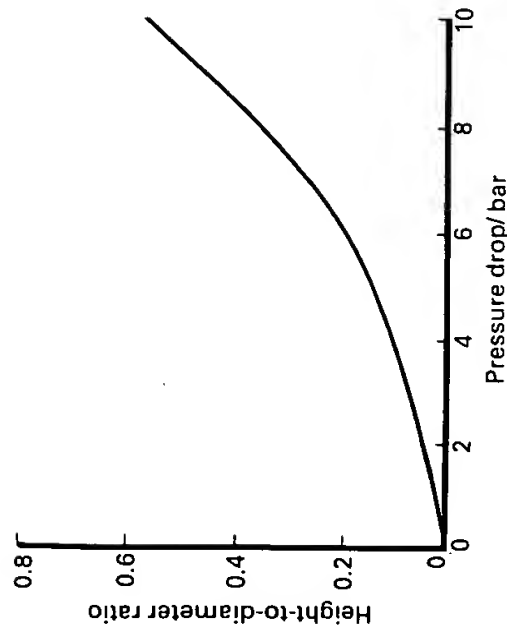Many operators use two beds of zinc oxide in series. This enables the

lead bed to be run to saturation before changing. This approach is particularly attractive to operators with high levels of sulphur in the feed, because by using a by-pass they can change each bed of zinc oxide without having to taking the plant off-line. Figure 4.12 shows the increase in hydrogen sulphide slip between two beds of zinc oxide used by an operator in the Middle East.[99]

4.11.8. Other Desulphurization Uses for Zinc Oxide

Zinc oxide absorbents were developed to remove hydrogen sulphide from hydrocarbons. It has been found that simple organic sulphur compounds are also removed by reaction with zinc oxide to form zinc sulphide, but this is via a cracking mechanism which leads to carbon deposition on the catalyst. This reaction is used by many operators during the start-up of a plant, when no hydrogen is available and the hydrodesulphurization catalyst is not functioning.

Zinc oxide is being used commercially to desulphurize carbon dioxide. For this application the temperature is below 100°C and the pressure up to 40 bar. Under these conditions zinc carbonate is stable and is formed first. The hydrogen sulphide reacts with the zinc carbonate to release carbon dioxide. The absorption profile for this duty are shown in Figure 4.13. Zinc oxide is also used for cyanide removal. Hydrogen cyanide reacts with zinc oxide at temperatures below 150°C to form zinc cyanide. At higher temperatures zinc oxide catalyses the decomposition of HCN.

Figure 4.13. The carbonate and sulphide profiles seen in a bed of zinc oxide (ICI Catalyst 32-4) used to desulphurize carbon dioxide at ambient temperature.

Figure 4.11. The relationship between pressure drop and height-to-diameter ratio for a bed of granular zinc oxide (ICI Catalyst 32-4). Temperature, 370°C; inlet pressure, 40 bar; feed, natural gas; flow rate, 29 000 N m³ h⁻¹; catalyst volume, 20 m³.
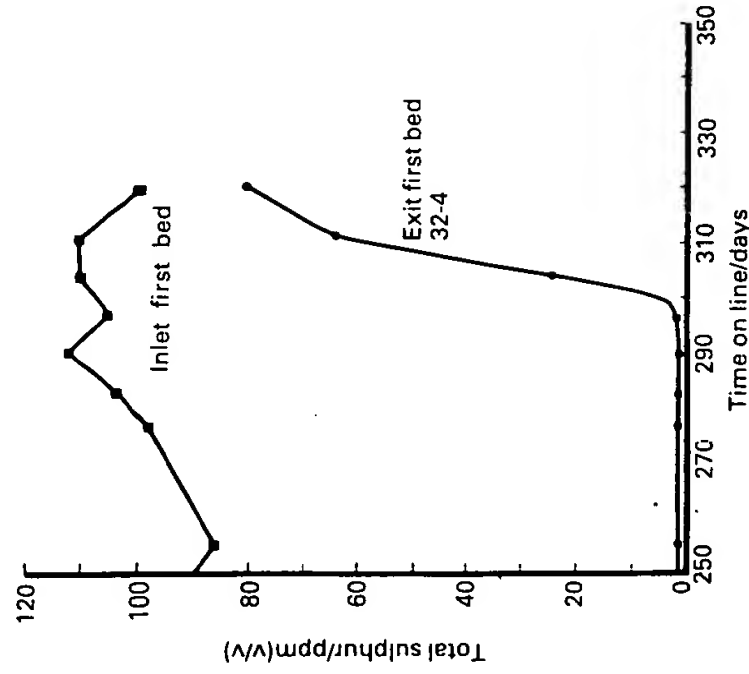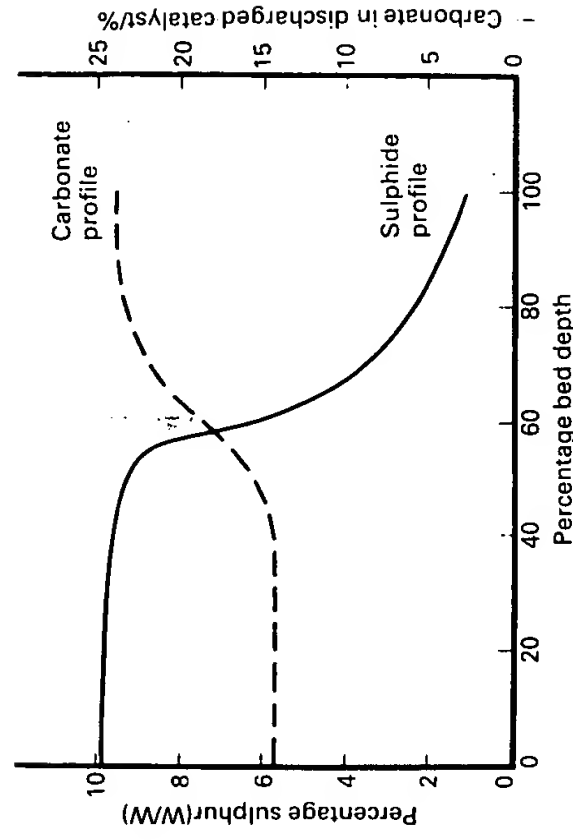

Figure 4.12. Inlet and interbed hydrogen sulphide concentration during the operation of two beds of zinc oxide in series (ICI Catalyst 32-4). Temperature, 370°C; pressure, 40 bar; space velocity, 1100 h⁻¹; catalyst volume, 18.5 m³.

Chapter 6). Chloride may be present in the process water, the air to the secondary reformer or the hydrocarbon feedstock. It is very difficult to remove chloride from the process air and, as a result, ammonia plants located near the sea or in heavily industrialized environments tend to have short LT shift catalyst lives. Modern water demineralization plants can effectively remove inorganic chlorides but cannot deal so well with organic chlorides, and plants using river water contaminated with pesticides may have problems with chloride poisoning. Reverse osmosis is used to deal with this problem in power stations, but is not really economical for ammonia plants with their high raw water make-up requirement.
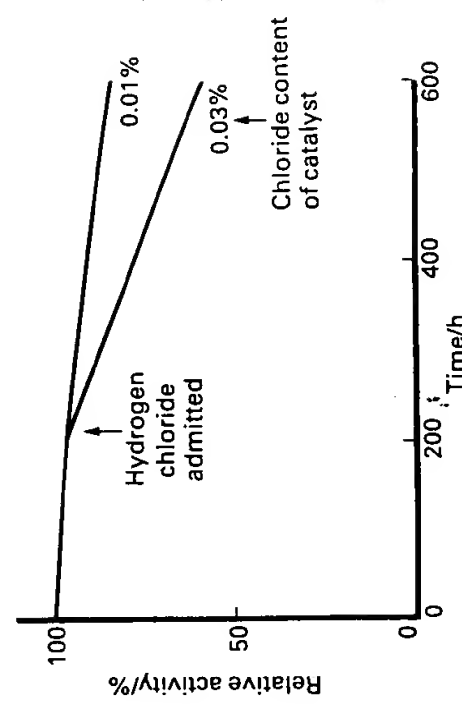

Figure 4.14. The effect of chlorine poisoning on the activity of low temperature shift catalyst (ICI Catalyst 53-1).

The increasing use of seawater injection to enhance oil production is resulting in higher levels of chloride in crude and distillate oils. Up to 15 ppm of aliphatic chlorides have been observed in naphtha fractions. Natural gas only rarely contains chlorides, but the use of rock caverns for storage of NGL and LPG can lead to hydrogen chloride in the gas. The level of hydrogen chloride increases with more dilute salt solution in contact with the liquid hydrocarbon.[101] One operator has found 0.3–0.5 $\mu g\,g^{-1}$ in feed gas being drawn from storage in a rock cavern.[102] Certain refinery processes give waste gases containing small amounts of hydrogen chloride. These gases are sometimes used as the feedstock for the related hydrogen reformer, and dechlorination has to be a stage of the refinery process. The arrival of a hydrocarbon feed, containing chloride, on a cobalt or nickel molybdate catalyst at the start of a normal purification train results in similar reactions to desulphurization. The organic chlorides are hydrogenolysed to give hydrogen chloride. If sulphur is present, then both hydrogen sulphide and hydrogen chloride

Zinc oxide has been widely used in guard beds to protect LT shift catalysts. Typical process conditions for this duty are about 200°C with a steam/gas ratio of 3 : 5 and an operating pressure of ~30 bar. Modern copper zinc LT shift catalysts are self-guarding, and it is better to use LT shift catalyst in the guard bed (see Chapter 6). Zinc oxide is, however, being used to protect methanation catalyst from being poisoned by sulphur compounds which can be carried over from certain carbon dioxide removal processes. Because the carry-over is transient and the total quantity of sulphur small, protection is obtained with a shallow layer of zinc oxide on top of the methanation catalyst. Typical process conditions are pressure ~20 bar, temperature 300°C and space velocity 25 000 h^{-1}.

4.11.9. Impurities in Zinc Oxide

Zinc ores usually contain arsenic, cadmium and lead compounds, so commercial zinc oxide may contain oxides of these metals. It has been found that arsenic and cadmium may be volatalized as sulphides and can be transferred from the zinc oxide. Arsenic is a severe poison to nickel reforming catalyst and the use of zinc oxide with a high level of arsenic (2000 ppm) has resulted in extensive damage to reforming catalyst.[100] Arsenic is a particularly serious poison because it first adheres to the pipework and is then slowly released onto the catalyst. Once arsenic has been deposited on the reformer tubes it can only be removed by mechanical cleaning. Cadmium is less of a problem than arsenic, as it does not have such a serious poisoning effect. It tends to migrate as far as the LT shift catalyst. Cadmium metal has been observed on cold parts of the reformer, such as the reformer tube ends. It is of particular importance to ensure that the zinc oxide installed in a plant is of proven quality and does not contain significant quantities of base metals.

4.12. Dechlorination

4.12.1. Chloride Sources and Absorbents

Chlorides are particularly severe poisons for copper-based catalysts such as low-temperature shift and methanol synthesis catalysts. The accumulation of even very small amounts of chloride has a very marked effect on catalyst activity. Figure 4.14 shows the results of introducing hydrochloric acid in the feed to a LT shift catalyst. An increase of chloride content of the catalyst from 0.01% to 0.03% halved the activity of the catalyst by accelerating the sintering of the active phases (see